# 3D polymer structures with variable permittivity at terahertz frequencies

Jonathan Hammler, Yi Pan, Andrew J. Gallant, and Claudio Balocco

School of Engineering and Computing Sciences, Durham University, South Road, Durham, DH1 3LE, United Kingdom

Abstract—Titanium dioxide (TiO<sub>2</sub>) powder has been blended with polydimethylsiloxane (PDMS) to manufacture a composite polymer with variable permittivity. Vector network analyser measurements taken between 0.75–1.1 THz quantify the relationship between TiO<sub>2</sub> concentration and complex permittivity of the resultant material. Complex 3D structures have been produced with a casting process. Applications for the tunable-permittivity polymer include dielectric regions in photonic and plasmonic devices operating at terahertz frequencies as well as single pixel imaging systems.

### I. INTRODUCTION

T ITANIUM dioxide  $(TiO_2)$  is used as a white colourant in paint, cosmetics, food colouring, etc. due to its large refractive index (n=2.4–2.8) [1] at visible wavelengths. This trait is maintained within the terahertz region of the electromagnetic spectrum. Similarly, polydimethylsiloxane (PDMS) is transparent in both visible and THz regions. This flexible silicone polymer is used to manufacture stamps for soft lithography, where feature sizes on the scale of tens of nanometers can be reproduced from moulds [2]. By mixing powdered TiO<sub>2</sub> into PDMS prior to curing, a composite material with increased permittivity is obtained. An investigation into the parameters determining complex permittivity of the material and its suitability for microfabricated devices has been performed.

### II. METHODOLOGY

The of ratio constituent component densities,  $\rho_{TiO_2}$ :  $\rho_{PDMS} = 4230$ : 1030 (kg/m<sup>3</sup>), was used to calculate the mass ratios required to result in total volume fractions of  $TiO_2$  equal to 0%, 10%, 20% and 30%. A batch of PDMS was manufactured by blending the base resin (Dow Corning SYLGARD 184) with the recommended quantity of curing agent (10% of base mass). Quantities of PDMS and  $TiO_2$ powder were then weighed with a sub-milligram precision balance prior to homogenisation. Magnetic stir plates were found to lack the torque required to adequately agitate the viscous resin mixture so mixing was performed by hand for five minutes. Dissolved air bubbles were extracted under hard vacuum before pouring the resin mixtures in to glass and aluminium moulds. Curing occured slowly at ambient temperature, 21°C, over 48 hours while under vacuum. Optical microscopy showed little indication of inhomogeneity of the sample surfaces.

Measurements were taken in the frequency range 0.75– 1.10 THz with a vector network analyser connected to frequency extension transceivers. Planar polymer samples were mounted orthonormal to the free space transmission path of



Fig. 1. Complex permittivity of cured polymer sample against fraction of volume occupied by titanium dioxide particles, where  $\epsilon_r = \epsilon_r' - j \epsilon_r''$ .  $f_c = 0.925$  THz.

Inset: Cast example structure, Durham University logo, composed of PDMS with  $\epsilon_r = 1.89$  and  $\epsilon_r = 3.13$ .

a collimated terahertz beam. The two port network was measured with the VNA after calibration. The complex permittivity of the materials under test was calculated from S-parameter data and geometric thickness with closed-form expressions [3] where the derivative of phase with respect to frequency is used to calculate the real component and the magnitude of transmission is used to find the imaginary component.

## III. RESULTS

The linear relationship between volume concentration of  $\text{TiO}_2$  and complex permittivity is shown in Figure 1. It has been found that an increased concentration results in an increase in both real and imaginary components of relative permittivity.

The dielectric properties of the composite are affected not just by ratio of pigment to binder, but by the quantities of each  $TiO_2$  polymorph (rutile, anatase and brookite) present in the powder; each one having a unique density and permittivity. Experimental results are compared with theoretical values [4] for mixtures of well defined constituent components. Homogeneity of the mixture is examined. Particle sizes of the pigment can range from tens of micrometers, as found in common food additives, down to tens of nanometers when specially prepared. Larger particles, with sizes of similar magnitude to the wavelength of incident terahertz radiation, create



Fig. 2. Phase shift mask generated from a Hadamard matrix of order 16, for coded aperture imaging in the THz region.  $\epsilon_r = 2.5$  throughout.

a stronger scattering effect than smaller particles resulting in an increasingly lossy material. All samples which have been prepared to date operate within the Mie scattering regime, with  $\alpha \approx 1.3$  found from analysis of scanning electron microscopy (SEM).

Figure 1 (inset) shows a cohesive structure with distinct three dimensional regions of differing permittivity:  $\epsilon'_r = 1.89$  in the clear region and  $\epsilon'_r = 3.13$  in the white area. The sample was manufactured by casting into a cavity mould. However, spin coating, stamping, screen printing or gravure printing techniques can also be used to produce patterned thin film

structures from the polymer.

Manufactured devices can serve as phase shift masks for THz coded aperture imaging as shown in Fig. 2, lenses, or as filters if a photonic band gap is introduced. The polymer can be used as a flexible substrate or bonded to several different surfaces including silicon, glass and aluminium. Metalisation of the polymer surface is also possible, to create dielectricmetal interfaces for plasmonic devices, (partially) reflecting mirrors or electrical contacts.

# IV. SUMMARY

A composite polymer with selectable dielectic constant at terahertz frequencies has been presented. The material has been shaped into complex 3D structures with applications in THz imaging systems. Further research will investigate rheological properties of the composite polymer and realising designs for THz lenses and including sensing structures within microfluidic cavities.

### REFERENCES

- L. J. Berberich and M. E. Bell, "The Dielectric Properties of the Rutile Form of TiO<sub>2</sub>," *Journal of Applied Physics*, vol. 11, pp. 681–692, Oct. 1940.
- [2] J. A. Rogers and R. G. Nuzzo, "Recent progress in soft lithography," *Materials Today*, vol. 8, no. 2, pp. 50–56, 2005.
- [3] A. Kazemipour, M. Hudlicka, T. Kleine-Ostmann, and T. Schrader, "A reliable simple method to extract the intrinsic material properties in millimeter/sub-millimeter wave domain," in *Proc. Conf. Precision Electromagnetic Measurements*, Rio de Janeiro, BR, Aug. 2014, pp. 576– 577.
- [4] J. A. Reynolds and J. M. Hough, "Formulae for dielectric constant of mixtures," *Proceedings of the Physical Society. Section B*, vol. 70, no. 8, pp. 769–774, 1957.